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Morphology-dependent gas-sensing sensitivity of γ -Al₂O₃ for methacrolein

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ABSTRACT

Methacrolein (MACR) is a key precursor in the formation of secondary organic aerosols and a significant occupational chemical hazard, posing risks to both the environment and health. In this work, three types of γ -Al₂O₃ were synthesized via hydrothermal methods, including nanorods, nanosheets, and a mixed morphology. Characterization results revealed that rod-like γ -Al₂O₃ has the largest specific surface area and the highest oxygen vacancy content. The possible formation mechanism of γ -Al₂O₃ samples with different morphologies was discussed. Further study indicated that the morphology of γ -Al₂O₃ significantly affects its sensitivity in the cataluminescence (CTL) sensing of MACR, with rod-like γ -Al₂O₃ exhibiting the highest sensitivity, whereas sheet-like γ -Al₂O₃ showed the lowest sensitivity. Thus, a CTL sensor based on rod-like γ -Al₂O₃ for MACR detection was developed, demonstrating outstanding performance in terms of sensitivity, reproducibility, and stability. This sensor was applied to the analysis of real samples, and the results were compared with those obtained by gas chromatography. The results obtained by the two methods were consistent, with relative error ranged from -4.0% to -4.9%. The sensing mechanism was further elucidated via density functional theory calculations, in situ Fourier transform infrared spectroscopy and gas chromatography-mass spectrometry. This work broadens the horizons for applying material science principles to enhance the performance of gas sensors, thereby contributing to design high-performance CTL sensors for air quality and occupational safety monitoring.

1. Introduction

Volatile organic compounds (VOCs) are of concern as both outdoor air pollutants and as indoor air pollutants. The main concern outdoors is the potential for VOCs to adversely impact the environment, due to they cause many reactions and disturb the chemical balance [1]. Particularly, some VOCs can undergo atmospheric oxidation with ozone, nitrate, and hydroxyl radicals to form secondary organic aerosol (SOA), which has a strong negative impact on human health and influence on climate [2,3]. While VOCs can also be a health concern indoors, due to exposure to VOCs can cause a range of possible harmful health effects such as respiratory failure, vasodilation, hypotension, convulsions, and paralysis [4]. Therefore, VOCs detection is of great significance for environmental safety and human health.

Methacrolein (MACR) is one of the more concerning VOCs. On the one hand, it is a key intermediate in the SOA formation from isoprene

oxidation, which plays an important role in atmospheric chemistry [5]. Isoprene is the most abundant nonmethane hydrocarbon emitted in the atmosphere, and its atmospheric photooxidation is one of the largest sources of SOA at a global scale. Although the underlying mechanism of SOA formation by isoprene remain unclear, intensive researches showed that MACR is a major first-generation isoprene oxidation product that act as an important SOA precursor [6]. In addition, MACR also is predominantly emitted from vegetation and anthropogenic activities such as gasoline vehicle emission, which also contributes to the formation of SOA [7]. Therefore, MACR holds a pivotal role in atmospheric chemistry, especially in urban and forested areas, where its contribution to SOA formation is particularly significant. On the other hand, MACR is an important chemical for the manufacture of methyl methacrylate and a key monomer in many polymerization reactions. MACR is a pulmonary irritant, which causes acute lung injury and pulmonary edema [8]. Therefore, the development of simple, rapid, and cheap methods for

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Received 18 May 2024; Received in revised form 9 July 2024; Accepted 16 July 2024 Available online 17 July 2024 0925-4005/© 2024 Elsevier B.V. All rights are reserved, including those for text and data mining, AI training, and similar technologies. on-line monitoring of MACR is essential for controlling air pollution and preventing occupational diseases.

Gas sensors represent a practical and cost-effective solution for the on-line monitoring of VOCs. To date, many gas sensors were designed to detect VOCs such as formaldehyde [9], acetone [10,11], benzene [12], and methanol [13] etc. Compared to gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS), gas sensors offer the advantages of real-time monitoring, portability, cost-effectiveness, and ease of use, making them particularly suited for rapid on-site detection [14]. Especially, the development of gas sensor based on cataluminescence (CTL) has attracted increasing attention. CTL is a type of chemiluminescence that occurs when a substance undergoes catalytic oxidation on the surface of a suitable catalyst, resulting in the emission of light [15–17]. The intensity of the emitted light is often proportional to the gas concentration, making CTL is an effective technology for gas detection. CTL-based gas sensors offer a unique combination of sensitivity, selectivity, and rapid response [18-21]. While CTL sensors generally require simpler instrumentation compared to advanced analytical techniques such as GC, GC-MS, and Fourier transform infrared (FTIR) gas analyzers, they still provide effective performance for on-line gas detection.

The application of CTL-based gas sensors is particularly fascinating, especially in environmental monitoring, industrial safety, and occupational health monitoring [22]. For instance, Li et al. developed a CTL sensor using Ce(IV)-MOF for hydrogen sulfide detection [23]. Lu et al. reported a CTL sensor based on hydrotalcite-supported gold nanoparticles, which shows potential for analyzing acetaldehyde in fruit beverages with minimized interferences [24]. Huang's group developed a novel multidimensional ratiometric CTL sensing strategy to detect and discriminate multiple organophosphate flame retardants, highlighting the potential of CTL sensors for rapid on-site detection of emerging contaminants [25]. Recently, our group developed a CTL sensor based on Y2O3 nanoparticles for detecting methyl ethyl ketone peroxide, achieving a detection limit of 1 ppb [26]. This work offers a promising approach for occupational safety and public-security monitoring. However, to our knowledge, there are currently no reports of CTL sensors specifically for MACR detection.

The sensing material is central to the design of high-performance gas sensors. To better facilitate practical applications, there are two issues continue to merit attention. Firstly, although the scope of gas sensing material has been greatly expanded [27], sensing material with simple structure but exhibits excellent performances is desired. Such sensing material offers the merits of low-cost, controlled preparation and scalable production. Secondly, the sensing performance is closely related to the morphology of sensing materials [28,29]. Giving an insight into the effects of sensing material morphology on sensing performance is beneficial to design gas sensors with excellent sensing performances [30].

Herein, three different morphologies of nanosized y-Al₂O₃ include nanorods, nanosheets and a mixture of nanorods and nanosheets were synthesized by simple hydrothermal methods using different surfactants. It is found that the nanosized γ -Al₂O₃ with different morphologies show different CTL response toward MACR, and rod-like γ -Al₂O₃ displays the highest response. A CTL gas sensor based on rod-like γ -Al₂O₃ was developed for on-line detection of MACR. The present sensor showed advantages of high sensitivity and selectivity, fast response time, short recovery time, and good reproducibility. The possible formation mechanism of γ -Al₂O₃ samples with different morphologies were discussed, and the sensing mechanism was also investigated. γ -Al₂O₃ is a widely utilized catalyst known for its ease of preparation and costeffectiveness. In this study, nanosized γ -Al₂O₃ was employed as the sensing material for the design of a MACR sensor, instead of complex structural materials. The synthesis methods involve a straightforward hydrothermal process under mild conditions, allowing for controlled preparation of γ -Al₂O₃ with different morphologies. These factors facilitate commercialization and practical application of the sensors.

2. Experimental section

2.1. Chemicals and apparatus

The detailed information on the chemicals and apparatus was listed in the Supplementary Material.

2.2. Preparation of γ -Al₂O₃ with different morphologies

Three kinds of nanosized γ -Al₂O₃ with different morphologies were synthesized using simple hydrothermal methods with different surfactants, followed by heat treatment. The procedures are described as follows and illustrated in Fig. 1. Firstly, 0.0113 g Aluminium nitrate nonahydrate (Al(NO₃)₃·9 H₂O) and 1.2 g NaOH were dissolved in 30 mL of alcohol-water mixed solution (2 mL n-butanol and 28 mL deionized water). The above solution was prepared in triplicate. Subsequently, 0.2 g of polyethylene glycol-2000 (PEG-2000), 0.36 g of cetyl trimethyl ammonium bromide (CTAB) or 0.26 g of sodium citrate were added to the three aforementioned solutions, respectively. These solutions were then vigorously stirred for 10 minutes. Afterwards, 3 mL ethyl acetate was added into the above solutions. After 20 min of magnetic stirring at room temperature, the mixed solutions were transferred into 100 mL Teflon-lined stainless steel autoclaves and maintained at 180 °C for 24 h, and then cooled down to room temperature. The white precipitates were collected by centrifugation, washed several times with anhydrous ethanol and deionized water, and then directly dried in an oven at 80 °C. Finally, γ -Al₂O₃ samples were obtained by annealing the precursors at 500 °C 3 hours in a vacuum muffle furnace under a vacuum level of -0.1 MPa. The resulting γ -Al₂O₃ samples were designated as γ -Al₂O₃-I, γ -Al₂O₃-II and γ -Al₂O₃-III, respectively.

2.3. Fabrication of sensor system

The design of the sensor system was similar to our previous work [26], and the schematic diagram is shown in Fig. S1. Briefly, the as-prepared nanosized γ -Al₂O₃ powders were dispersed in deionized water to form a suspension, which was then coated onto the surface of a ceramic heater. The ceramic heater was placed inside a quartz reactor equipped with gas inlets and outlets. The quartz reactor was positioned above the PMT detector, and an optical filter with a selectable wavelength range of 350–505 nm (bandwidth: 24 nm) was inserted between the reactor and the PMT to reduce background radiation and select the analytical wavelength. The operating temperature of the sensor was controlled by adjusting the input voltage to the ceramic heating tube. An automated gas sampling process was achieved by using a 6-port sampling valve equipped with a sample loop. A syringe pump was used to inject liquid organic reagents into a heated tube to produce standard gases. An air generator was used for providing the carrier and dilution gases of standard gases. The flow rates of the gases were controlled by mass flow controllers. A BPCL ultraweak luminescence analyzer was used to record and process the optical signals.

2.4. Method for the preparation of standard gases

Ammonia, nitric oxide, nitrogen dioxide, sulfur dioxide, carbon monoxide, and hydrogen sulfide are commercially available as standard gases. Before use, these gases are diluted to the desired concentrations using clean dry air provided by an air generator. For the dilution process, the flow rates of the dilution air and standard gases were precisely controlled using mass flow controllers, ensuring that they were mixed in specific ratios to achieve the desired concentrations of the target gases. Other standard gas samples such as MACR, *n*-butyraldehyde, propionaldehyde, ethanol, acetone and so on are generated through the evaporation of liquid reagents. The liquid organic reagents are injected into a heating tube via a syringe pump, where they were vaporized and mixed with a diluent gas, then carried into the sampling valve. The



Fig. 1. The synthesis processes of three different morphologies of γ -Al₂O₃.

temperature of the heating tube was set approximately 5 °C higher than the boiling points of the organic compounds, and the evaporation temperature for MACR set at 75 °C. The concentration of the standard gas can be controlled by adjusting the flow rate of diluent gas and the injection rate of the syringe pump, and calculated through equation:

$$c = \frac{\omega \nu \rho}{F} \times 10^3 \tag{1}$$

where *c* (mg/m³) is the gas concentration; ω (%) is the purity of the liquid organic reagent, ρ (kg/m³) denotes the density of organic reagent; ν (µL/min) and *F* (mL/min) represent the injection rate of the syringe pump and the flow rate of the diluent gas, respectively. When it was necessary to change the type of gas, 1 mL of deionized water was injected into the heating tube by the syringe pump, and the diluent gas flow rate was set to 2 L/min to flush out the residues in the tubing. After this flushing procedure, blank tests were conducted by running the sensor system with only the diluent gas and checking for any residual signals. If residual signals were detected, the system was flushed again, and the residual signals were detected, ensuring that the system was completely free of any previous residues before introducing a new gas.

2.5. Procedure for gas sensing

In the present work, clean dry air was used as the carrier gas, and all sensing measurements were conducted in an air atmosphere. Taking the γ -Al₂O₃-I sensor as an example, the measurement procedure is as follows: Before the measurement begins, the flow rate of the carrier gas was set to 622 mL/min, and the working temperature was raised to 400 °C. The sensor was then calcined in the air stream for 10 minutes to activate the catalyst and remove adsorbates. Subsequently, the working temperature was reduced to an appropriate value, and measurement was taken after baseline was stable. It typically takes about 2 minutes for the sensor to stabilize after changing the temperature. This duration ensures that the baseline signal is steady and that the sensor is ready for reliable readings. The negative high voltage of PMT was set to -800 V, with a measurement interval of 0.5 s.

2.6. Experimental design for sample analysis

MACR and other organic reagents were stored in a fume hood with their caps slightly loosened, and air samples from within the hood were collected into 1 L sampling bags using an air sampler under exhaust condition. In total of three samples were collected. The MACR concentration in the samples was determined using both the sensor and gas chromatograph-flame ionization detector (GC-FID) equipped with sixway valve. The GC conditions are listed in Table S1, and the GC calibration curve for MACR is depicted in Fig. S2. To facilitate simultaneous measurements of the same sample using two different methods, the sixport valve of the sensor was connected in series with the six-port valve of the gas chromatograph. The specific connection method is depicted in Fig. S3. An air sampling pump is utilized to draw the sample from the sampling bag into the six-port valves.

2.7. Methods for mechanism study

Intermediates produced in the course of MACR oxidation on γ -Al₂O₃ were identified by in-situ FTIR spectroscopy. An in-situ diffuse reflectance cell was used for measurements. The γ -Al₂O₃ sample as pressed into self-supported discs and placed in a sample holder at the center of the cell. The temperature of the cell was controlled by a temperature controller. After adjusting the in-situ cell to the desired temperature, a steady stream of MACR gas at a concentration of 180 mg/m³ (flow rate of 2.3 L/min) was continuously introduced into the cell. Data collection begins after stabilizing for 10 minutes. The spectra were collected by recording 4 scans at a resolution of 4 cm⁻¹.

GC-MS was employed to further investigate the oxidation reactions of MACR on γ -Al₂O₃ surface. MACR at a concentration of 180 mg/m³ was collected in a 1 mL polytetrafluoroethylene (PTFE) sampling bag. As depicted in Fig. S4, to collect the exhaust gas after the MACR reaction, a PTFE tube was used to connect the sampling bag to the inlet of the air sampling pump. The outlet of the pump was connected to the inlet of the quartz reactor, and the outlet of the quartz reactor was connected to another sampling bag. After setting the working temperature to 187 °C, the MACR gas was passed over the γ -Al₂O₃ surface under the action of the air pump to facilitate the reaction. The flow rate of the sampling pump was set to 622 mL/min. A 0.5 mL sample was extracted for analysis, with GC-MS conditions detailed in Table S2. After adjusting the working temperature to 187 °C, the MACR gas was made to pass over the γ -Al₂O₃ surface under the action of the air pump to induce the reaction. A 0.5 mL sample was extracted for analysis, with GC-MS conditions outlined in Table S2.

The computational results discussed in this study were obtained using the Dmol3 package [31]. Considering the exchange-correlation functional, the generalized gradient approximation with the Perdew-Burke-Ernzerhof function was selected [32]. The double-numeric polarized basis set was chosen, and the density functional theory (DFT) semi-core pseudopotential was adopted which includes the norm-conserving pseudopotential and the relativistic effect to treat the core electrons. To guarantee the cutoff radius was larger enough, the value was set of 4.5 Å. Geometric optimization was firstly carried out to obtain the adsorption structure with the minimum total energy. The convergence criteria of geometric optimization were set as 1×10^{-5} Ha for total energy, 0.004 Ha/Å for maximum force of every atom, and 0.005 Å for maximum displacement. The electronic self-consistent field tolerance was set at 10^{-5} Ha. A $3 \times 3 \times 1$ Monkhorst-Pack grid k-point was set in geometric optimization with smearing of 0.005 eV. The adsorption energy E_{ads} was calculated using the following equation:

$$E_{\rm ads} = E_{\rm total} - E_{\rm surface} - E_{\rm gas} \tag{2}$$

where E_{total} represents the total energy of the gas molecules on the γ -Al₂O₃ surface system, E_{surface} and E_{gas} represent the energies of the γ -Al₂O₃ surface and isolated molecules, respectively. The smaller E_{ads} is, the easier the gas adsorbed.

3. Results and discussion

3.1. Material characterization

The crystalline structures of these as-prepared sample were investigated by XRD. As shown in Fig. 2 A, five diffraction peaks of the asprepared materials at $2\theta = 31.9^{\circ}$, 37.0° , 39.4° , 45.7° , 66.7° can be indexed to the (220), (311), (222), (400) and (440) planes of cubic γ -Al₂O₃ with lattice constants of a = b = c = 7.9 Å (JCPDS No. 10–0425), indicating that the phase structures of the all as-prepared materials are γ phase of Al₂O₃ [33]. Moreover, no impurity peaks are present, obviously proving that all the as-prepared γ -Al₂O₃ were highly purified.

The EPR measurements were performed to investigate the oxygen vacancies in the γ -Al₂O₃ samples. As shown in Fig. 2B, all the three γ -Al₂O₃ samples display a symmetrical EPR signal at g = 2.002, which further manifest the presence of O_V. The intensity sequence of EPR signals also indicates that γ -Al₂O₃-I contains the highest concentration of O_V, followed by γ -Al₂O₃-II, and γ -Al₂O₃-III has the least.

The surface chemical composition and chemical state of the three γ -Al₂O₃ nanomaterials were investigated by XPS. As shown in Fig. 3A, signals of Al and O are all observed in the XPS survey scan spectra of three γ -Al₂O₃ samples, and no any other elements are present except C which was assigned as a reference, indicating that highly purified γ -Al₂O₃ samples are synthesized successfully. The high resolution O1s spectra of all γ -Al₂O₃ samples are shown in Fig. 3B-D. The O 1 s spectra of all the samples can be deconvoluted into three peaks. The peak at lower binding energy (BE) at \sim 530.38 eV is assigned to the lattice oxygen (O_a), a second peak at ~531.40 eV is ascribed to chemisorbed oxygen (O_{β}), and a small peak at ~532.50 eV indicates the existence of surface hydroxyl groups (O_y) [34]. The concentration of oxygen vacancy (O_V) can be evaluated according to the ratio of $O_\beta/(O_\alpha + O_\beta + O_\gamma)$ [35, 36]. As shown in Table S3, the O_V concentration ranks in the following order: γ -Al₂O₃-I (46.54 %) > γ -Al₂O₃-II (41.62 %) > γ -Al₂O₃-III (38.58 %), suggesting that γ -Al₂O₃-I has more oxygen vacancies. This observation is consistent with the EPR results. Surface vacancies tend to adsorb and activate gaseous O₂ to form adsorbed oxygen species, which has been proved can enhanced sensing sensitivity [37,38].

The morphology of the three γ -Al₂O₃ samples were characterized by TEM. The γ -Al₂O₃-I predominantly consists of nanorods (Fig. 4A), while γ -Al₂O₃-II comprises a mixture of nanosheets and nanorods (Fig. 4D), with nanosheets being more abundant than nanorods. The γ -Al₂O₃-I sample exclusively contains nanosheets (Fig. 4G). Lattice fringes with 0.19 nm interplanar spacing assigned to (400) is found in high-resolution TEM (HRTEM) images (Fig. 4B, E and H) of all γ -Al₂O₃ samples. The selected area electron diffraction (SAED) patterns (Fig. 4C, F and I) of all samples exhibit diffraction rings consisting of discrete diffraction spots, indicating polycrystalline nature of cubic γ -Al₂O₃. In the SAED images of the three γ -Al₂O₃, the first ring belongs to the (400) plane with $d_{440} = 0.1395$ nm, which are well in agreement with the XRD results.

The Brunauer–Emmett–Teller analysis and the UV–vis DRS of the γ -Al₂O₃ samples were determined, the results are shown in Fig. S5 and Fig. S6, respectively. The detailed discussion also can be seen in the Supplementary Material.

3.2. Formation mechanism

The type of surfactant significantly influences the morphology due to their varying functional group types and lengths, diverse ionized state in the solution, and the differences in intrinsic electric fields. The possible formation mechanism of γ -Al₂O₃ samples with different morphologies is detailed in the Supplementary Material and the schematic is depicted in



Fig. 2. (A). XRD patterns of the γ -Al₂O₃ samples. (B). EPR spectra of the γ -Al₂O₃ samples.



Fig. 3. (A) Low-resolution survey spectra of the three γ -Al₂O₃ samples. (B-D) High-resolution XPS spectra of O 1 s of the γ -Al₂O₃-I, γ -Al₂O₃-II and γ -Al₂O₃-II.

Fig. S7.

3.3. Optimization of the sensing conditions

The analytical wavelength (λ , nm), working temperature (T, °C) and flow rate (F, mL/min) of carrier gas are crucial parameters for CTL sensing, interacting to influence sensitivity. Response surface methodology (RSM) was employed to optimize parameters for MACR sensing. Because the infrared background radiation emitted by the ceramic heater increases with the wavelength or temperature, signal to noise ratio (S/N) was used to study the optimal conditions of CTL sensors using the three as-prepared γ -Al₂O₃ samples for sensing of MACR. A three-factor and three-level Box-Behnken text was design was conducted by using the Design-Expert software. Three-dimensional (3D) plots as shown in Fig. S8 were constructed to visualize the interaction effects of independent variables (λ , T and F) on S/N, showing these independent variables have significant influences on the S/N of all three sensor, with the existence of optimal conditions at which the S/N attains its maximum value. The predicted optimal conditions and corresponding S/N values provide by RSM are shown in Table S4. Verification experiments were performed to confirm the predicted values. As shown in Table S4, the experimental S/N values correlated well with the predicted S/N values with acceptable errors, indicating predicted optimal conditions are reasonable.

3.4. Gas-sensing properties

The Table S4 reveals that the three types of γ -Al₂O₃ possess the same optimal detection wavelength (425 nm) and working temperature (187

°C), yet they differ in their optimal flow rates. The optimal flow rates of carrier gas for γ -Al₂O₃-I, γ -Al₂O₃-II, and γ -Al₂O₃-III are 622, 490, and 460 mL/min, respectively. Thus, the response of the three γ -Al₂O₃ to MACR was assessed under flow rates of 622, 490, and 460 mL/min, to investigate the sensing sensitivity. As depicted in Fig. 5A, all three γ -Al₂O₃ exhibited the highest CTL intensity and *S*/*N* at their own optimal flow rates. Notably, the order of both CTL intensity and *S*/*N*, across varying flow rates, consistently remained as: γ -Al₂O₃-I > γ -Al₂O₃-II > γ -Al₂O₃-II.

CTL emission is emitted by heterogeneous catalytic oxidation, which proceeds at the interface of the solid catalyst and the gas phase. As illustrated in Fig. 5B, the CTL reaction mainly proceeds through four steps, including gas diffusion, adsorption, surface catalytic reaction, and desorption. The total reaction rate is depended on the rate-determining step. If the rate of diffusion is faster than that of the surface catalytic reaction, the total reaction rate is limited by the surface reaction. In such cases, increasing the carrier gas flow rate does not effectively enhance the reaction rate. Conversely, if the rate of the surface catalytic reaction exceeds the diffusion rate, the diffusion rate becomes the ratedetermining step; hence, an increase in flow rate of carrier gas can improve the diffusion rate, subsequently boosting the reaction rate. At the same working temperature, the optimal flow rates for the three types of γ -Al₂O₃ are in the order of γ -Al₂O₃-I > γ -Al₂O₃-II > γ -Al₂O₃-III. This also demonstrates that γ -Al₂O₃-I possesses the highest catalytic activity, making it the preferred choice for developing a CTL sensor dedicated to MACR detection.

Selectivity is a crucial performance criteria of gas sensor. In order to assess the selectivity of CTL sensor based on γ -Al₂O₃, 180 mg/m³ of MACR, *n*-butyraldehyde, propionaldehyde, ethanol, acetone, methanol,



Fig. 4. TEM images (A, D, C), HRTEM images (B, E, H) and SAED patterns (C, F, I) of γ -Al₂O₃-I (A, B, C), γ -Al₂O₃-II (D, E, F), and γ -Al₂O₃-III (G, H, I).

n-hexane, formaldehyde, formic acid, acetic acid, ethyl acetate, benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, phenylacetaldehyde, and isoprene, as well as 1000 ppmv of ammonia (759 mg/m³), nitric oxide (1339 mg/m³), nitrogen dioxide (2054 mg/m³), sulfur dioxide (2857 mg/m³), carbon monoxide (1250 mg/m³) and hydrogen sulfide (1517 mg/m³) were detected at a working temperature of 180 °C, a detection wavelength of 425 nm, and a flow rate of 622 mL/min,. As shown in Fig. 6 A, MACR produces a strong response, whereas *n*-butyraldehyde, propionaldehyde and ethanol generate only weak responses, with their response intensities not exceeding one-tenth of that for MACR. Other gases cannot produce any response. This indicates that the γ -Al₂O₃ exhibits excellent selectivity towards MACR.

To evaluate the reproducibility of the γ -Al₂O₃-I sensor, ten parallel measurements of MACR at a concentration of 180 mg/m³ were conducted under optimal conditions (working temperature of 180 °C, detection wavelength of 425 nm, flow rate of 622 mL/min). As shown in Fig. 6B, the γ -Al₂O₃-I sensor has no obvious change in response after ten cycles with a relative standard deviation (RSD) of 2.0 %. Subsequently, the stability of the γ -Al₂O₃-I sensor was assessed by measuring MACR at 180 mg/m³ continuously over seven days. As depicted in Fig. 6 C, the RSD of the response signal over seven days is 2.7 %. These results indicate that the γ -Al₂O₃-I sensor possesses excellent reproducibility and stability.

The dynamic property of the sensor is evaluated using the response time (t_{RES}) and recovery time (t_{REC}). In this study, the response time is defined as the duration required for the sensor signal to reach its peak value after the introduction of the sample. The recovery time is defined as the time it takes for the signal to return from its peak value to the baseline level. Fig. 6D presents the dynamic response-recovery curves response curves of the γ -Al₂O₃-I sensor to MACR at concentrations of 180, 283, and 567 mg/m³ under a reaction temperature of 187 °C. The

 $t_{\rm RES}$ and $t_{\rm REC}$ do not significantly change with variations in MACR concentration, remaining approximately 2 s and 30 s, respectively. This indicates that the γ -Al₂O₃-I sensor possesses rapid response and recovery capabilities. With excellent reproducibility and stability, as well as rapid response and recovery capabilities, the γ -Al₂O₃-I sensor is quite suitable for the on-line rapid sensing of MACR.

At a working temperature of 180 °C, a detection wavelength of 425 nm, and a flow rate of 622 mL/min, the relationship between the CTL response and MACR concentration was investigated. As illustrated in Fig. 6E, the CTL response increases with the concentration of MACR. Further investigation reveals a good linear relationship between the CTL response and MACR concentration within the range of $40-1300 \text{ mg/m}^3$ (13–415 ppmv). The linear regression equation is I = 28.35c - 1837, where I represents the CTL response, and c denotes the concentration of MACR. The detection limit is 15 mg/m³ (4.8 ppmv) at an S/N of 3. The National Institute for Occupational Safety and Health (NIOSH) has established a permissible immediately dangerous to life or health (IDLH) concentration for MACR at 50 mg/m³ (16 ppmv). The detection limit of the γ -Al₂O₃-I sensor is below this threshold, suggesting that it is suitable for detecting elevated concentrations of MACR in industrial or occupational settings. However, the concentration of MACR in outdoor ambient air is typically low, usually at the ppb level [39,40]. Even when using mass spectrometry, long preconcentration operations are required to meet sensitivity requirements [41]. The detection limit of the γ -Al₂O₃-I sensor is at the ppm level, which limits its applicability for monitoring MACR in outdoor ambient air to some extent.

3.5. Sample analysis

To assess the practical utility of this sensor, air samples containing MACR were determined by both the sensor and GC. The results from the



Fig. 5. (A) Dynamic response-recovery curves of three γ -Al₂O₃ to MACR at different flow rates. γ -Al₂O₃-I (pale yellow), γ -Al₂O₃-II (light green), γ -Al₂O₃-III (light purple). Insets: The *S*/*N* of three γ -Al₂O₃ to MACR at different flow rates. The concentration of MACR is 180 mg/m³, detection wavelength is 425 nm, working temperature is 187 °C. (B) Schematic of fundamental steps of a typical CTL process.

GC method are considered the true values, while those from the sensor are regarded as the measured values. As shown in Table S5, the relative error ranged from -4.0 % to -4.9 %, demonstrating that the capability of the sensor for practical applications.

3.6. Mechanism study

Active sites of the sensing material play a crucial role in gas sensing. These sites are specific locations on the surface of the material where adsorption and subsequent reactions of target gas molecules occur. Sensing material with a large specific surface area usually has more active sites. The γ -Al₂O₃-I sample has largest specific surface area and exhibits highest sensitivity. However, the specific surface area is not the only factor that influences these active sites. The O_V on sensing material surface can act as the active site for molecule adsorption and generation of reactive oxygen species [42]. Due to the (400) and (440) planes are the exposed facets of γ -Al₂O₃, to explore the impact of O_V on the sensing performance of, density functional theory (DFT) calculations were performed to evaluate the adsorption energy of oxygen molecules on both the pristine and oxygen-deficient (400) and (440) planes of γ -Al₂O₃. As illustrated in Fig. 7 A, compared to the pristine planes, the adsorption energy of oxygen on the defective planes is more negative, indicating that oxygen molecules are more readily adsorbed onto the defective surfaces. Furthermore, the O-O bond distance of adsorbed oxygen on the defective surfaces is increased. The O-O bond distance of adsorbed oxygen on pristine (400) and (440) planes are 1.41 and 1.38 Å, whereas in the oxygen-deficient (400) and (440) facets, the O-O bond distance of adsorbed oxygen extend to 1.55 and 1.50 Å. The elongation of the O-O bond length indicates that molecular oxygen is more readily dissociated to form chemisorbed oxygen species $(O_2^-, O^- \text{ and } O^{2-})$, thereby enhancing the sensing performance. The sequence of O_V content in the three types of γ -Al₂O₃ is γ -Al₂O₃-I > γ -Al₂O₃-II > γ -Al₂O₃-III, which is consistent with the sequence of sensing sensitivity. This further illustrates the significant role of O_V in influencing the sensing sensitivity.

Additionally, the abundance of active exposed facets also has a significant impact on the sensing performance. From the thermodynamics point of view, the surface energy of an individual nanosheet with two main exposed planes is quite high, leading nanosheets to aggregate perpendicularly to the surface planes to decrease the surface energy by reducing exposed areas [43]. Consequently, the abundance of exposed reactive planes in sheet-like γ -Al₂O₃ may decrease. This could potentially explain why the sensitivity of sheet-like γ -Al₂O₃ is lower than that of rod- like γ -Al₂O₃.

As illustrated in Fig. 5B, the adsorption of gas molecules is a key step in the CTL reaction process. The adsorption properties of different gas molecules on the surface of the sensing material can directly affect the selectivity of the sensor. To confirm the above deduction, the adsorption energies of methanol, ethanol, *n*-butyraldehyde propionaldehyde, and MACR on the oxygen-deficient (400) and (440) planes of γ -Al₂O₃ were calculated. The calculated adsorption configurations and the adsorption energies as shown in Fig. 7B. For each gas, the adsorption energy on the oxygen-deficient (400) plane is stronger than that on the oxygendeficient (440) plane. The order of adsorption strength is MACR > *n*butyraldehyde > propionaldehyde > ethanol > methanol, which is highly consistent with the order of response signal intensity of these gases on the sensor surface (Fig. 6 A). This suggests that the high selectivity of γ -Al₂O₃ for MACR may be partially attributed to MACR being the most readily adsorbed on the γ -Al₂O₃ surface.

To further investigate the CTL mechanism of MACR on the γ -Al₂O₃ surface, in-situ FTIR spectra of γ -Al₂O₃ exposed to MACR under the pressure of O₂ were measured to study the behavior of reaction process. As seen in Fig. 7 C, the exposure of γ -Al₂O₃ at room temperature to



Fig. 6. (A) The response of different gases on the γ -Al₂O₃-I sensor. (B) continuous response-recovery curves of the γ -Al₂O₃-I sensor toward 180 mg/m³ of MACR. (C) The CTL response within one week. (D) The dynamic response-recovery curves of γ -Al₂O₃-I sensor toward different concentrations of MACR. (E) The CTL responses of the γ -Al₂O₃-I sensor towards different concentrations of MACR under the optimal conditions. Inset: Calibration curve between CTL response and MACR concentration. Error bar stand for \pm SD (n = 3). Working temperature is 187 °C, detection wavelength is 425 nm, flow rate is 622 mL/min.



Fig. 7. (A) The adsorption configurations and the adsorption energies of O_2 on (400) and (440) planes without and with O_V . (B) The adsorption configurations and the adsorption energies of different gas molecules on the on (400) and (440) planes without and with O_V . (400)- O_V and (440)- O_V stand for oxygen-deficient (400) and (440) planes. (C) In-situ FTIR spectra of MACR over γ -Al₂ O_3 at different temperatures.

MACR shows strong absorbance bands at 2963, 2935, 2872, 1689, and 1313 cm⁻¹. Absorption band at 1689 cm⁻¹ is assigned to C=O stretching vibrations of unsaturated aldehydes, and absorption bands between 2800–3000 cm⁻¹ are attributed to aliphatic C–H stretching vibrations. When the temperature is increased from room temperature to 187 °C, new absorption bands appear, and the absorption bands of MACR at 1689 cm⁻¹ and 1314 cm⁻¹ are significantly reduced. This indicates that the adsorbed MACR can be transformed into new species on the heated γ -Al₂O₃ surface.

The presence of O_V on the γ -Al₂O₃ surface leads to the formation of coordinatively unsaturated aluminum atoms, which act as Lewis acid sites. These sites can bind with hydroxyl groups, existing as Al-OH_{ads} species, which play a significant role in the catalytic activity of γ -Al₂O₃ [44,45]. Chen et al. studied the reaction process of MACR on α -Al₂O₃ surfaces using FT-IR spectroscopy [46], and the FT-IR spectra reported by them are highly similar to those obtained in this study. They also suggested that the in dry air the clean a-Al2O3 surface with OV is dominated by aluminum atoms showing Lewis acidic properties, then surface-active oxygen on surface can attack adsorbed MACR molecules, leading to the formation of formaldehyde and propionaldehyde. These compounds are then oxidized to produce formic acid and propionic acid, respectively. Our experimental results show newly emerging absorption bands between 1700–1740 cm⁻¹, which are associated with C=O stretching vibrations, indicating that aliphatic carbonyl compounds are significant products of the reaction of MACR, as supported by reference 46. The absorption bands in the $1350-1600 \text{ cm}^{-1}$ are associated with carboxylates adsorbed on the oxide surface, characterized by strong absorption at 1550–1600 cm⁻¹, and often showing peak splitting or multiple adsorption peaks at $1350-1410 \text{ cm}^{-1}$ [47]. Specifically, the peaks at 1588 cm⁻¹ and 1372 cm⁻¹ can be attributed to the asymmetric and symmetric stretching vibrations of COO group for formate species, while those at 1563 cm⁻¹ and 1460 cm⁻¹ can be assigned to COO group for propionate species [46,48]. A new absorption peak at 2352 cm⁻¹ corresponds to the asymmetric stretching vibration of CO2 linearly adsorbed on cationic sites [49], indicating that carboxylic species may be further oxidized to produce CO₂. The peaks at 3726 cm⁻¹ and 3682 cm⁻¹ correspond to the stretching vibrations of free and adsorbed hydroxyl groups [50], respectively.

To further explore the reaction mechanism, GC-MS was used to identify the products of MACR on the γ -Al₂O₃ surface. The sample passed over unheated γ -Al₂O₃ surface acted as a blank sample, and both MACR and CO₂ were detected. The detected CO₂ at this time may originate from ambient air, introduced during the sampling or syringe injection process. When MACR passed over the γ -Al₂O₃ surface heated to 187 °C, only unreacted MACR and CO2 were detected, with no other products identified. The exhaust gas collected in the sampling bag was repeatedly passed over the heated CO2 surface for analysis, and even after 20 cycles, only unreacted MACR and carbon dioxide were still detected. As shown in Fig. S9, with increasing number of cycles, the concentration of MACR gradually decreased while that of CO2 increased (after deducting background CO₂), indicating that MACR ultimately decomposes to form CO₂, which is consistent with the in-situ FTIR results. However, other aldehydes and acids were not detected by GC-MS, likely because these compounds undergo rapid reactions on the γ -Al₂O₃ surface and require in-situ detection techniques to effectively capture their presence. At 187 °C, O⁻ ions are the predominant form of chemisorbed oxygen [51]. Based on the aforementioned observations, the potential reactions of MACR on the γ -Al₂O₃ surface are as follows:

$$O_{2(gas)} \rightarrow O_{2(abs)}$$
 (3)

$$O_{2(abs)} + 2e^- \rightarrow 20^- \tag{4}$$

$$CH_{2} = C(CH_{3})CHO_{ads} + O^{-} + 2Al-OH_{abs} \rightarrow HCHO_{abs} + CH_{3}CH_{2}CHO_{abs} + 2Al-O_{abs} + e^{-}$$
(5)

$$HCHO_{abs} + O^{-} \rightarrow H - HC(O)O_{ads} + e^{-}$$
(6)

$$CH_{3}CH_{2}CHO_{abs} + O^{-} \rightarrow CH_{3}CH_{2} - HCOO_{ads} + e^{-}$$
(7)

$$H-HC(O)O_{ads} + O^{-} \rightarrow H-C(O)O_{ads} + OH_{ads} + e^{-}$$
(8)

$$CH_3CH_2 - HCOO_{ads} + O^- \rightarrow CH_3CH_2 - C(O)O_{ads} + OH_{ads} + e^-$$
(9)

$$2H-C(O)O_{ads} + O^{-} \rightarrow 2CO_2 + H_2O + e^{-}$$
(10)

$$2CH_{3}CH_{2}-C(O)O_{ads} + 13O^{-} \rightarrow 6CO_{2} + 5H_{2}O + 13e^{-}$$
(11)

$$Al-O_{abs} + OH_{ads} + e^{-} \rightarrow Al-OH_{abs} + O^{-}$$
 (12)

The overall reaction can be represented as:

$$CH_2 = C(CH_3)CHO + 5O_2 \rightarrow 5CO_2 + 3H_2O$$
 (13)

Reaction 5 illustrates the crucial role of Lewis acid sites in the catalytic oxidation process. Increasing O_V can produce more active Lewis acid sites, which further illustrates the significant impact of O_V content on sensor sensitivity. According to classical theory, the oxidation of MACR on the γ -Al₂O₃ surface requires the formation of luminescent intermediates to produce CTL emission. However, luminescent intermediates are highly unstable and difficult to detect. In the future, more advanced techniques will be required to further investigate the CTL mechanism of MACR.

4. Conclusion

In summary, three different morphologies of nanoscale γ -Al₂O₃, namely nanorods, nanosheets, and their mixed morphology counterparts, were synthesized by using different surfactants. Experimental results indicated that rod-like γ -Al₂O₃ exhibited the highest sensitivity to MACR. The CTL sensor based on rod-like y-Al2O3 for MACR showed advantages of high sensitivity, good selectivity, rapid response/recovery speed, and excellent stability. The mechanism study has deepened the understanding of the sensing mechanism, highlighting the significance of surface morphology and oxygen vacancies in enhancing the CTL response. This study not only provides a novel approach for the rapid monitoring of MACR, but also offers valuable insights into designing high-performance CTL sensors. Future research should focus on further enhancing sensitivity by tailoring the morphology, optimizing the oxygen vacancy content, or incorporating additional materials. These approaches will be crucial for achieving lower detection limits and expanding the sensor's applicability to a broader range of real-world scenarios.

CRediT authorship contribution statement

Yuchun Chen: Visualization, Software. Qingsong Chen: Resources, Funding acquisition, Formal analysis. Quanquan Gong: Supervision, Funding acquisition. Taicheng An: Writing – review & editing, Supervision, Project administration, Conceptualization. Kaihui Li: Visualization, Investigation, Formal analysis. Jintian Tang: Visualization, Validation, Data curation. Jiajian Liu: Writing – original draft, Visualization, Software, Investigation. Runkun Zhang: Writing – original draft, Visualization, Methodology, Investigation, Funding acquisition, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.snb.2024.136323.

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